Hydrocracking Reaction of n-Hexadecane Using Nickel-Natural Zeolite Catalyst and Determination of Activation Energy (Ea) and Reaction Order

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Abstract: Research has been carried out on the preparation of active natural zeolite impregnated with nickel followed by activity testing through the hydrocracking catalytic reaction of n-Hexadecane. Active natural zeolite was obtained from PT Prima Zeolita Yogyakarta. The nickel concentration in the zeolite sample was carried out by ion exchange method with [Ni(NH₃)₆]²⁺ precursor solution with a concentration of 0.06M. The nickel content of the catalyst was determined by Atomic Absorption Spectrophotometer (AAS). The hydrocracking reaction used a fixed bed reactor system. Ratio of feed (n-Hexadecane) : catalyst = 3 : 1 (in gram). Catalysis study also carried out at various temperatures, from 315°C - 450°C at certain nickel content. The results of the catalytic reaction at each temperature after passing through the cooling system there was a liquid fraction that had been successfully accommodated then weighed and determined the percent of conversion. Furthermore, for the determination of Ea and the order of the reaction using linear regression calculations. The results showed that the catalytic reaction using an active natural Ni-Zeolite catalyst in the n-Hexadecane hydrocracking process resulted in different conversion results depending on the temperature of the catalytic reaction. The largest conversion was obtained at a temperature of 450°C, which was 35.18%. The reaction order was the first-order reaction (n=1). Meanwhile, the activation energy or activation energy (Ea) of the catalytic reaction in the n-Hexadecane hydrocracking process using a natural Ni-Natural zeolite catalyst with a nickel content of 2.0% (w/w) was 127.071 kJmol⁻¹.

Keywords: Natural zeolite; Catalyst; Hydrocracking; Activation energy; Reaction order

Introduction

The use of catalysts and carriers from zeolite is expected to provide more selective, more optimal results and provide results with greater economic value. This will result in different results if the conversion process is carried out without catalyst and carrier. In conversion without a carrier catalyst known as thermal cracking, the process to produce the desired product will work at high operating temperatures and pressures and will have an impact on large operating costs (less economical) and the results may be less selective. As it is known that zeolite is the most commonly used carrier material today. This carrier material can be found according to the formation process as synthetic zeolite and natural zeolite. Natural zeolites have different impurity content and type from one place to another where natural zeolites are found.

Vansant (1990), concluded that in general zeolite can be defined as an alumina-silica crystal with a hollow tetrahedral basic framework structure. which can contain cations and water molecules that are free to move. Zeolite consists of alumina groups and silica-
oxide groups, each of which is tetrahedral in shape and is interconnected by oxygen atoms in such a way as to form a three-dimensional framework. The presence of cavities or pores distributed in the zeolite will be related and have a direct effect on the surface area.

Today, with the development of the petroleum refining industry and the petrochemical industry as well as various other downstream industries in Indonesia, it will require a variety of catalysts and carriers that are more specific to the carrier of zeolite to carry out chemical processes. Catalysts are generally defined as substances that can speed up a chemical reaction into products. Transition metals are metals that are commonly used as catalysts, either in the form of pure metals, metal oxides, or carrier metals. One of the references is to find out how good the catalyst is necessary to determine the energy of its activity (Kadarwati et al, 2013; Amilia et al, 2015).

To determine the energy of activity, it can be carried out, among others, a natural zeolite catalyst accompanied by nickel metal. Next, a catalytic reaction is carried out, for example, the catalytic reaction of n-Hexadecane, namely a straight-chain alkane as a model that will show the occurrence of catalytic reaction in the hydrocracking process. The hydrocracking reaction is an exothermic reaction without a change in the number of molecules. The hydrocracking process is a catalytic hydrocarbon cracking process by injection of hydrogen at the desired temperature and pressure to get a reaction product that has a lower molecular weight.

In general, this hydrocracking process can be used to convert medium distillate, heavy distillate, and deasphalted oil into gasoline, kerosene, and diesel oil. Arroyo et al, (2000) observed the process of hydrocracking and isomerization of a mixture of n-paraffin and gas oil using a Pt/ZSM-22 catalyst. From the results of this study, it was reported that there was a process of breaking the C-C bond at the beta (β) position in the hydrocracking process. Joo et al, (1997) used a zeolite catalyst with a combination of Ni-Mo metal as a hydrocracking catalyst for plastic pyrolysis results. This research succeeded in converting the plastic components into naphtha components. Scherer and Richer, (1978), suggested that the use of zeolite Y has high selectivity in the cracking of petroleum (Hegedus, 1985). Isoda et al (1998), have developed Ni, Co, and Fe metals into zeolite Y which is used as a catalyst for hydrocracking of C15-C32 chain hydrocarbon compounds and aromatic rings with 3-4 members in vacuum gas oil. From the results of the study, it was reported that the Ni-Y catalyst was able to convert C15-C32 chain hydrocarbons and aromatic rings with 3-4 members better than the zeolite Y catalyst with impregnated metals Co and Fe. Transition metals are metals that can function directly as catalyst without being charged first on the carrier but has weaknesses, including a relatively small surface area, and during the catalytic process, clumping can occur (Trisunaryanti et al, 2005). In the hydrocracking process, the catalysts commonly used are heterogeneous. Ni metal is a transition metal in the periodic system as used by Isoda et al(1998) as a catalyst in zeolite Y. Zeolite ZSM-22 and zeolite Y described above are synthetic zeolites that can be made from the main ingredients, namely free silica and alumina. In the zeolite synthesized, the impurity content is almost non-existent. Suyati et al, (2007), used Ni/active natural zeolite catalyst for hydrocracking of coal tar. The phenomena of catalyst deactivation and the effects of regeneration method on the characteristics and activity of Ni/Natural zeolite catalyst after being used in continuous cracking reaction of polypropylene have been studied (Khabib et al,2014). The manufacture of fraction gasoline, among others, were carried out by Salim et al (2016), using Ni/modified natural zeolite for hydrocracking of coconut oil, Salamah et al (2022), hydrocracking waste cooking oil using a Ni catalyst impregnated on mesoporous silica synthesized from Beach Sand and obtained gasoline fraction. Aziz et al, (2021), cracked crude biodiesel into biodiesel using NiO/active natural zeolite catalyst. Ramadani et al, (2017), used Ni/active natural zeolite ataylst for the manufacture of biodiesel from ketapang seed oil. In contrast to natural zeolites, the content is very heterogeneous and contains many impurities other than the basic framework which does not function as a catalyst. Natural zeolites are mixed with impurities other than zeolite minerals, which can be either crystalline or amorphous (Trisunaryanti et al, 1996). It was also stated that natural zeolite is generally found in mixed form with other types of zeolite and with amorphous minerals such as feldspar, silica, clay, as well as transition metal oxides, and organic contaminants (Lee et al., 2002). Thus, natural zeolite is a heterogeneous system, and to maximize its use as a catalyst, the heterogeneous system needs to remove impurities other than the basic framework.

Generally, what is done to obtain natural zeolite with high capability is for example being used as a catalyst or carrier for metal catalysts through treatment in the form of activation of natural zeolite. Physical activation is in the form of heating. Meanwhile, chemical activation using an acid solution aims to clean the surface of the pores, removing impurities such as organic compounds and other amorphous materials so that it will increase the surface area. Impurities from organic materials, amorphous or crystalline materials that do not function as catalysts or catalyst carriers need to be removed or removed from the natural zeolite.

The raw materials used in this hydrocracking process are very flexible, ranging from light to heavy fractions, including naphtha fraction, gas fraction, and...
vacuum distillate. The total hydrogen requirement in the hydrocracking process depends on the type of raw material being processed and the type of product desired. The position of the catalyst in the reactor is fixed (fixed bed). The raw material that has become a gas phase and continues to be injected with hydrogen gas will pass through the catalyst until a catalytic reaction occurs to produce a product.

Acid sites on catalysts such as nickel zeolite catalysts can produce cracking products. If the acid site is getting stronger it will produce cracking products high too. The rate of a reaction can be defined as the change in concentration per unit time or a decrease in the concentration of the reactants per unit time. For example, a first-order reaction:

\[
A \xrightarrow{k} B
\]

Then the reaction rate is:

\[
\frac{dc}{dt} = -kc
\]  

Where : c = concentration of A  
 k = reaction rate constant

In the catalytic reaction to determine the rate of reaction used flow method (Moore, 1981). The flow method is the best way to detect very fast reactions where the reagents are not mixed before entering the reactor. The basic equation for the plug flow reactor, derived from a tabular reactor with a constant cross-sectional area A as shown in Figure 1 shows that the steady flow u is expressed as a volume per unit time.

\[
\frac{dn_i}{dt} = dV - ud_i c_i
\]  

After a steady-state is reached, the concentration of each component in each volume element becomes constant. The composition from one unit to the next is different. In steady-state applies:

\[
r_i dV = u d_i c_i
\]  

This form when integrated gives the following results:

\[
\frac{V}{u} = \int f_{co} \frac{dc_i}{r_i}
\]  

Where co is the concentration of the component ai that enters the reaction chamber and V is the volume of the reactor that is passed by the reactant with a concentration of c.

In a catalytic reaction in a reactor with a fixed position of the catalyst, the volume is the bulk volume (v). From equation in (1) substituted into equation (4) and integrated gives the result:

\[
k = \frac{u}{V} \ln \frac{co}{c}
\]  

This equation can also be written as follows:

\[
k = \frac{u}{V} \ln \frac{1}{(1-x)}
\]  

where : k = reaction rate constant (min⁻¹); u = gas flow rate (mLmin⁻¹); V = bulk volume (mL); x = conversion

Knowing the value of the reaction rate constant (k), it will obtain information about the rate of a reactant into a product. When connected with other forms of the Arrhenius equation, namely:

\[
k = Ae^{-\frac{Ea}{RT}}
\]  

\[
lnk = -\frac{Ea}{RT} + lnA
\]  

So, from this equation assuming that the reaction of the n-hexadecane cracking process is first order, the activation energy (Ea) can be determined from the slope of the graph of ln k versus 1/T which the graph produces a straight line.

The activation energy (Ea) is considered constant with temperature variations. Slope = - Ea/R and intercept is A is an Arrhenius factor. Activation energy is the minimum energy required by reactants to form intermediates before reactants are converted into products. The presence of a catalyst is expected to reduce the activation energy (Ea) of a reaction before the reactants are converted into products.
The purpose of this study was to determine the total conversion, the order of the catalytic reaction in the n-hexadecane hydrocracking process, to determine the activation energy (Ea) of the nickel catalyst carried or impregnated in an active natural zeolite (Ni-ZAA) after the catalytic reaction was carried out in the hydrocracking process of n-Hexadecane.

Method

Instrumentation
Porcelain cup, balance scale, a set of reactors (for activation test), AAS (Atomic adsorption Spectrophotometry) Nippon Jarrel Ash AA-782, Gas Chromatography–Mass Spectroscopy (GC-MS) Shimadzu QP 5000, other glassware.

Materials
Active natural zeolite from PT Prima Zeolita Yogyakarta, Aquades, whatman paper 42, Ammonium nitrate (E. Merck), Nickel(II) nitrate hexahydrate (E. Merck), n-Hexadecane (E. Merck), Glass Wool, ethanol (E. Merck).

Procedure
Preparation of H-Zeolite
1. Active natural zeolite (ZAA) was ground and then sieved to obtain particles with a size smaller than 250 mesh.
2. The active natural zeolite sample was heated to a temperature of 250°C for 5 hours after this temperature was reached.
3. Then the sample was allowed to cool, then immersed in a 1.5M NH₄NO₃ solution and stirred for 24 hours, then the sample was washed with sufficient distilled water.
4. After the washing water was removed, the sample was heated to dryness in an oven at 130°C.
5. Sample was calcined at 500°C for 4 hours in the furnace, so that H-Zeolite was obtained.

Impregnation of Nickel on H-Zeolite
Nickel metal impregnated on the carrier (zeolite) which can be done with way of ion exchange (Augustine, 1990). In ion exchange, nickel metal is obtained from the nitrate salt solution of Ni(NO₃)₂·6(H₂O). Then it is converted into the form of hexamin nickel (II) or [Ni(NH₃)₆]²⁺ complexes as exchange cations. The nickel (II) hexamin ion form can be trapped more stable in the zeolite because the radius size becomes larger than before in the nickel (II) hexamin ion form. The procedure is as follows:
1. Samples of H-Zeolite (immersed in a nickel (II) hexamin ion complex solution, at concentration of 0.06M.
2. Next, the mixture was stirred for 24 hours, then filtered.

3. After that the mixture was dried, then put into the reactor to be calcined and flowed with nitrogen gas for 5 hours at a temperature of 500°C then oxidized by flowing oxygen gas at a temperature of 400°C for 3 hours.
4. The next step was reduced by flowing hydrogen gas for 2 hours at a temperature of 350°C to get a nickel distribution with zero charge on the pore surface of the zeolite support material.
5. Next, the nickel determination test using AAS (Atomic Adsorption Spectrophotometry).

Activity Test of Catalyst
The raw material (n-paraffin/n-hexadecane) was put in a heat-resistant container, the catalyst was prepared and placed in the reactor, and then put in the furnace. The catalyst which was in a fixed position in the reactor was then heated to the temperature of 315°C. n-Hexadecane was heated while being injected or flowed with hydrogen gas continuously at a flow rate of 200 mL/min. After the raw material evaporates, it would pass through the catalyst which had been heated at the above temperature. The ratio of raw material and catalyst 3:1 (in grams).

The result of the catalytic reaction in the hydrocracking process has then flowed in a cooler so that it was liquid. Furthermore, the result was accommodated in a container which has been weighed and the weight was known. Furthermore, the weight of the container and the liquid that was successfully accommodated weighing was done. The difference was the weight of the liquid that has been successfully accommodated by the hydrocracking process. In the next stage, the liquid was further analyzed. Then did the repetition. The following hydrocracking processes were treated at 365°C, 415°C, and 450°C, respectively. To calculate the conversion (%) expressed by the following formulation (Arroyo et al, 2000):

\[
Xi = \frac{Fi_o - Fi}{Fi_o}
\]  

Where:
- \(Xi\) = component conversion i
- \(Fi_o\) = initial weight or % original area
- \(Fi\) = weight that is not cracked.
  - or % of the remaining area that is not cracked.

Result and Discussion

Result of Determination of Nickel content and Activity Test of Catalyst

After the ion exchange was carried out through immersion of active natural zeolite with 0.06M precursor solution, the nickel content in the zeolite was...
determined and the nickel content was 2.0% (w/w), (abbreviated as Ni-ZAA2). Furthermore, the activity of the Ni-zeolite catalyst was tested.

The results of the activity test through the catalytic reaction in the hydrocracking process were obtained in the form of conversion of n-Hexadecane into parts that had a smaller number of C atoms than the number of C atoms of n-Hexadecane (C16).

In the hydrocracking process in this study, the catalytic reaction treatment was started at a temperature of 315°C. The boiling point of n-Hexadecane was 297°C so at 315°C it is expected that conversion has occurred. Hydrocracking results in the form of gas are passed through a cooling system until the results are obtained in liquid form. The results in liquid form were weighed and then compared with the initial weight of n-Hexadecane before the hydrocracking process. Furthermore, the conversion of n-hexadecane could be calculated by comparing the initial (n-hexadecane) feed which was the weight before the hydrocracking process, and the weight of the hydrocracking process that could be accommodated in liquid form as well as those that couldn't be accommodated in liquid form.

The analysis of the result of the liquid that was successfully accommodated using GC-MS to compare the results of the chromatogram contained in the feed (initial n-Hexadecane before being cracked) where the peak appeared at a retention time of 23.684 minutes. The peak of the remaining unconverted n-hexadecane appeared at the retention time of 23.684 minutes. The result of hydrocracking of n-Hexadecane using Ni-ZAA2 catalyst at a temperature of 315 °C produced conversion (%) of 0.33.

Furthermore, the temperature of the catalytic reaction was increased and the percent conversion was obtained as shown in the following Table. The resulting liquid was analyzed using GC-MS.

Table 1: Conversion (%) Liquid Yield Hydrocracking Process of n-Hexadecane Using Ni-ZAA2 Catalyst

<table>
<thead>
<tr>
<th>Temperature of Reaction (°C)</th>
<th>Weight of hydrocracking product that could be accommodated (g)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>315</td>
<td>2.65</td>
<td>0.33</td>
</tr>
<tr>
<td>365</td>
<td>2.59</td>
<td>1.20</td>
</tr>
<tr>
<td>415</td>
<td>2.27</td>
<td>2.24</td>
</tr>
<tr>
<td>450</td>
<td>1.58</td>
<td>0.51</td>
</tr>
</tbody>
</table>

From the data in Table 1 above, it can be seen that for the above temperature interval the n-hexadecane hydrocracking process results in a conversion that tends to increase in value, but if you look at the results of the hydrocracking process that can be accommodated after passing through the cooling system, it can be predicted that there would be some results of hydrocracking process which could be converted to a liquid state. The indication could also be seen from the results of the hydrocracking process which is accommodated in liquid form, the weight decreased with increasing the temperature of the catalytic reaction.

Based on the GC-MS chromatogram data, the liquid produced by the hydrocracking process at a temperature of 365°C with the conversion of 1.20% for Ni-active natural zeolite catalyst with code Ni-ZAA2. Three kinds of compounds/fractions were obtained. The three kinds of compounds/fractions were 

C10H22, C11H24, and C14H30 with compound codes numbered 3, 4, and 6, respectively as shown in Figure 2.

At this temperature, the GC-MS results for the liquid that has been successfully accommodated by the hydrocracking process shows a product that is entirely straight chain. From the graph in Figure 2 above, it can be seen that the C14H30 fraction is wider than the other fractions. This means that the C14H30 fraction is more dominant in the liquid that has been successfully accommodated as a result of the hydrocracking process. In the Ni-Natural zeolite catalyst with the code Ni-ZAA2 at a temperature of 365°C, when considered with the part of the hydrocracking process that was not successfully accommodated as a liquid with the cooling system used where the conversion reached 2%, it could be predicted that there was a smaller fraction of C10 that had not been detected. It can be seen that n-Hexadecane has a total of 16 C atoms (C16).

In the Ni-ZAA2 catalyst the dominant fraction was C14H30 which was the result of the cleavage of the number two of C atom (β). As it has been stated that the hydrocracking product using zeolite will not produce or produce very little carbon chain double bonds. This phenomenon is in accordance with Gates (1979) research that zeolite catalysts produce more alkane molecules.

The following table 2 is the conversion of the results that cannot be accommodated calculated gravimetrically so that in the end the total conversion can be calculated.
From the gravimetric calculation data mentioned above seems like there was an enhancement in n-Hexadecane conversion as the temperature of the catalytic reaction increased. In the presence of some of the results of the hydrocracking process which cannot be dispersed after passing through the cooling system used, it should be taken into account as an indication of conversion as well. At a temperature of 450°C, the conversion increased to 34.67%. Table 3 below is the total conversion data, namely adding up the conversions calculated gravimetrically due to the hydrocracking process that couldn't be accommodated as a liquid after it was passed through the cooling system with the conversion value obtained from the gas that was successfully accommodated as a liquid after analysis using GC-MS.

<table>
<thead>
<tr>
<th>Temperature of Reaction (°C)</th>
<th>Conversion result using GC-MS (%)</th>
<th>Conversion result Gravimetrically (%)</th>
<th>Total Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>315</td>
<td>0.33</td>
<td>0.00</td>
<td>0.33</td>
</tr>
<tr>
<td>365</td>
<td>1.20</td>
<td>2.00</td>
<td>3.20</td>
</tr>
<tr>
<td>415</td>
<td>2.24</td>
<td>12.67</td>
<td>14.91</td>
</tr>
<tr>
<td>450</td>
<td>0.51</td>
<td>34.67</td>
<td>35.18</td>
</tr>
</tbody>
</table>

The results of determining the total conversion using a natural Ni-zeolite catalyst in the n-Hexadecane hydrocracking process showed the presence of improvement total conversion along with increasing catalytic reaction temperature. In the total conversion of natural Ni-Zeolite catalysts, it can be seen that the low conversion value up to a temperature of 450°C could be caused by the heterogeneity contained in natural zeolites other than the basic framework. In natural zeolite there are a number of impurities (other components besides the framework) which can affect the conversion of n-Hexadecane into compounds with shorter of C chain.

**Result of Determination of Activity Energy (Ea) and Reaction Order (n)**

The results of determining the rate constant (k) using equation (6) are shown in table 4 below.

<table>
<thead>
<tr>
<th>Temperature of Reaction (°C)</th>
<th>Total Conversion (% of Hexadecane)</th>
<th>Constant of Rate Reaction (k) (men-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>315</td>
<td>0.0033</td>
<td>0.4400</td>
</tr>
<tr>
<td>365</td>
<td>0.0320</td>
<td>4.3364</td>
</tr>
<tr>
<td>415</td>
<td>0.1491</td>
<td>21.5281</td>
</tr>
<tr>
<td>450</td>
<td>0.3518</td>
<td>57.8280</td>
</tr>
</tbody>
</table>
From Figure 3, it can be seen that based on the appearance of the image the reaction is first order (n=1) this can be seen from the graphic form. Previous research conducted by Suyati, (2000) showed that the cracking reaction was a first-order reaction. The reaction order referred to here was the reaction order for disconnection (cracking) straight-chain hydrocarbon compound of n-Hexadecane using Ni-ZAA2 catalyst into a fraction of the carbon chain that was shorter than the original. This graph also obtained Ea (activation energy) using the equation Slope = -Ea/R. From this equation, Ea was obtained for the natural Ni-Zeolite catalytic reaction on the hydrocracking of straight-chain compounds from n-Hexadecane of 127.071 kJmol-1. This value also describes the minimum energy required by the reactants using Ni-ZAA2 catalyst to form intermediate compounds before the reactants are converted into products. This higher energy requirement could be caused by the heterogeneity of the constituents of natural zeolite other than the basic framework, whose presence can interfere or cause inhibition of the catalytic reaction. In addition, the position of the dispersed metal in the zeolite if there is accumulation will also affect the course of the catalytic reaction, which causes contact with the reactants not to be optimal. This metal accumulation can be caused by the large average pore radius in natural zeolite and small specific surface area in the natural zeolite.

Conclusion

The total conversion of n-Hexadecene hydrocracking reaction using Ni-ZAA2 catalyst was 35.18% with the dominant fraction is C₄H₉O for hydrocracking results that could be accommodated and analyzed by GC-MS. The catalytic reaction using Ni-ZAA2 catalyst in the n-Hexadecene hydrocracking process was first-order reaction (n=1). The activation energy (Ea) of the catalytic reaction in the hydrocracking process of n-Hexadecane using Ni-Active natural zeolite catalyst was 127.071 kJmol⁻¹

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References


